Preface

Transition metal oxides and chalcogenides are an ideal platform for demonstrating and investigating many interesting electronic phases of matter. These phases emerge as a result of collective many body interactions among the electrons. The omnipresent electron, depending on its interaction with other electrons and with the underlying lattice, can generate diverse phases of matter with exotic physical properties. The ultimate objective of Materials Science is to provide a complete microscopic understanding of these myriad electronic phases of matter. A proper understanding of the collective quantum behavior of electrons in different system can also help in designing and tuning new electronic phases of matter that may have strong impact in the field of microelectronics, well beyond that predicted by Moore′s law.

Strong electron correlation effects produce a wide spectrum of ground state properties like superconductivity, Metal Insulator Transition (MIT), charge-orbital ordering and many more. Similarly, different spin interactions among electrons, essentially due to various kinds of exchange coupling, give rise to varying magnetic ground state properties like ferromagnetism, antiferromagnetism, spin glass, among others. The main objective of this thesis is to understand and rationalize diverse electronic and magnetic phases of matter in some selected strongly correlated systems.

In **chapter 1** we have provided an overview of various electronic and magnetic phases of matter which are relevant and necessary for understanding the chapters that follow. The first part of this chapter describes the fundamental concepts of the so called Metal Insulator Transition (MIT). A small section is dedicated to the subtle interactions among electrons and lattice that actually drive a system from a highly conducting metallic state to a strongly resistive insulating state. The second part of this chapter offers a compilation of different magnetic ground states which are discussed in detail in the last two chapters.

In **Chapter 2**, we have explained various methodologies and experimental techniques that have been used in the work reported in this thesis.

In **Chapter 3**, we have provided a detailed understanding of the MIT in different polymorphic forms of Vanadium dioxide (VO_2). Although VO_2 exhibits a number of polymorphic forms, only the rutile/monoclinic VO_2 phase has been studied extensively compared to other polymorphic forms. This phase shows a well established MIT across $\sim$340 K, which has been extensively investigated in order to understand the relative importance of many body electron correlation effects arising primarily from on-site Coulomb interactions within the Vanadium 3*d* manifold, and single electron effects in-

fluenced by the dimerization of Vanadium atoms. Unlike the rutile phase of VO_2, little is known about the MIT appearing across 212 K in the metastable B-phase of VO_2. This phase shows dimerization of only half of the Vanadium atoms in the insulating state, in contrast to rutile/monoclinic VO_2, which show complete dimerization. There is a long standing debate about the origin of the MIT in the rutile/monoclinic phase, that contrasts the role of the many-body Hubbard *U* term, with single particle effects of the dimerization. In light of this debate, the MIT in the B-phase offers a unique opportunity to understand and address the competition between many body and single particle effects, that has been unresolved over several decades. In this chapter we have investigated different polymorphs of VO_2 to understand the underlying electronic structure and the nature of the MIT in these polymorphic forms. The MIT in VO_2 B phase is very broad in nature. X-ray photoemission and optical conductivity data indicate that in case of VO_2 B phase both correlation effects and dimerization is necessary to drive the MIT. We have also established that the correlation effects are more prominent for VO_2 B phase compared to rutile/monoclinic phase.

In **Chapter 4**, we have discussed the electronic structure of $LaTiO_3$ (LTO)-$SrTiO_3$ (STO) system. At the interface between polar LTO and non-polar (STO) oxides, an unique two dimensional electron gas (2DEG) like state appears, that exhibits a phenomenal range of unexpected transport, magnetic, and electronic properties. Thus, this interface stands as a prospective candidate for not only fundamental scientific investigation, but also application in technological and ultimately commercial frontiers. In this chapter, using variable energy Hard X-ray photoemission spectroscopy (HAXPES), we have experimentally investigated the layer resolved evolution of electronic structure across the interface in LTO-STO system. HAXPES results suggest that the interface is more coherent in nature and the coherent to incoherent feature ratio changes significantly as we probe deeper into the layer.

In **chapter 5**, we have investigated the electronic structure of the chemically exfoliated trigonal phase of MoS_2. This elusive trigonal phase exists only as small patches on chemically exfoliated MoS_2, and is believed to control functioning of MoS_2 based devices. Its electronic structure is little understood, with total absence of any spectroscopic data, and contradictory claims from theoretical investigations. We have addressed this issue experimentally by studying the electronic structure of few layered chemically exfoliated MoS_2 systems using spatially resolved X-ray photoemission spectroscopy and micro Raman spectroscopy in conjunction with electronic structure calculations. We have established that the ground state of this unique trigonal phase is actually a small gap ($\sim$90 meV) semiconductor. This is in contrast with most of the claims in existing literature.

In **chapter 6**, we have reexamined and reevaluated the electronic structure of the late 3*d* transition metal monoxides (NiO, FeO, and CoO) using a combination of HAXPES and state-of-the-art theoretical calculations. We have observed a strong evolution in the valence band spectra as a function of excitation energy. Theoretical results show that a combined GW+LDA+DMFT scheme is essential for explaining the observed experimental findings. Additionally, variable temperature HAXPES measurements in-

dicate that the antiferromagnetic ordering of NiO has strong influence in Ni $2p$ core level spectra.

In **chapter 7**, we have tried to understand the magnetic ground state of Mn doped $SrTiO_3$ system. We have shown that the random doping of Mn in Ti site can introduce frustration. This frustration among Mn sites prevents any spin ordering even at very low temperatures, although a strong antiferromagnetic interaction can be observed from magnetic susceptibility measurements. AC susceptibility data unambiguously proves that no glassy state is present in this system and that all spins are dynamical down to very low temperatures. Specific heat data further indicates a spin liquid like ground state behavior in this system.

In **chapter 8**, we have differentiated the surface and the bulk electronic structure in Sr_2FeMoO_6 and also have provided a new route to increase the Curie temperature of this material. Sr_2FeMoO_6 is well known for its high Curie temperature (T_c $\sim$410 K), half-metallic ferromagnetism, and a spectacularly large tunneling magnetoresistance. The surface electronic structure of Sr_2FeMoO_6 is believed to be different from the bulk; leading to a Spin-Valve type Magnetoresistance. We have carried out variable energy HAXPES on Sr_2FeMoO_6 to probe electronic structure as a function of surface depth. Our experimental results indicate that surface is more Mo^{6+} rich. We have also demonstrated what we believe is the first direct experimental evidence of hard ferromagnetism in the surface layer using X Ray Magnetic Circular Dichroism (XMCD) with dual detection mode. In the second part of this chapter we have designed a new route to increase the Curie temperature and have been successfully able to achieve a Curie temperature as high as 515 K.